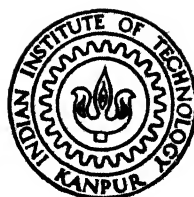


# STUDY ON THE AGEING OF RADIOACTIVE SULFIDE SOLUTION

by  
A. KANDA SAMY

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NUCLEAR ENGINEERING AND TECHNOLOGY PROGRAMME  
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR

JANUARY, 1982

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A Thesis Submitted  
in Partial Fulfilment of the Requirements  
for the Degree of  
MASTER OF TECHNOLOGY

by  
A. KANDA SAMY

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INDIAN INSTITUTE OF TECHNOLOGY, KANPUR  
JANUARY, 1982

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NETP-1902-M-SAM-STU

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CERTIFICATE

This is to certify that this work entitled  
"STUDY ON THE AGEING OF RADIOACTIVE SULFIDE SOLUTION"  
has been carried out by Mr. A. Kandasamy under my  
supervision and it has not been submitted elsewhere  
for a degree.

January, 1982

*Shankar Mukherji*  
Shankar Mukherji  
Thesis Supervisor

ACKNOWLEDGEMENT

I am highly indebted to Professor Shankar Mukherji for introducing me to Nuclear Chemistry and later for his active guidance throughout the course of my thesis work.

I would like to express my heartfelt thanks to Professor K. Sri Ram for his helpful suggestions throughout my course work and research work.

More than a word of thanks goes to Mr. S.N. Muddukrishna for the help and discussion during this work. It is nice to have him as my colleague in the laboratory. Without him I would have felt alone in the lab.

Finally I would like to thank Mr. J.P. Gupta for elegant typing and R.S. Tripathi for neat cyclostyling.

( A. KANDASAMY )

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ABSTRACT

Solutions of  $S^{2-}$  are known to undergo chemical transformation on keeping in air for long periods of time. Some workers have reported the presence of  $SO_3^{2-}$  and  $S_2O_3^{2-}$  as the major products.  $\gamma$ -radiolysis of  $S^{2-}$  solutions also leads to the same products. Solutions of  $S^{2-}$  containing radioactive  $^{35}S$  has been also known to undergo oxidative and radiolytic changes with  $SO_3^{2-}$  as the product. Since radioactive  $^{35}S^{2-}$  is used in various experiments on the assumption that it is pure  $^{35}S^{2-}$  it is necessary to test this assumption in view of the possible radiolytic changes it may undergo as a function of its age.

Conventional chemical analysis is usually carried out by adding milligram quantities of the expected radiolytic/oxidative products as inactive carriers, then chemically separating them and estimating their amounts by the measurement of radioactivity by a suitable counter. The main drawback in using this procedure is our lack of knowledge of the number and nature of the possible products. In this work the investigation consists of (a) setting up of a convenient and suitable procedure for determining the number of possible products and (b) a method of identifying them.

In this work, an anion-exchange column has been used for the separation of sulfur products. At least one sulfur product

is present corresponding to each peak obtained by plotting the eluted activity per 1.4 ml against the eluant volume. Elution conditions were studied and calibrations were done using both inactive and radioactive solutions.

Comparison of the experimental results obtained with 7-day old  $^{35}\text{S}^{2-}$  solution and four month old  $^{35}\text{S}^{2-}$  solution indicates that within a period of four months most of the original sulfide has undergone conversion into other products in addition to  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$ .

## CHAPTER 1

### INTRODUCTION

This work represents an investigation of the oxidation states of sulfur in a solution which originally consisted of pure sodium sulfide containing radioactive  $^{35}\text{S}$ . Radioactive isotopes, either with carriers or in carrier-free states, are available commercially from the major nuclear facilities of the world. These isotopes are mainly used as tracers for a variety of purposes<sup>1-3</sup>. Since extremely small number of radioactive atoms can be detected quantitatively through their radioactivity and as the chemical properties of the radioactive isotope is identical with those of the inactive ones, radioisotopes are used widely to study the mechanisms of chemical reaction<sup>4</sup>, biological degradation, synthetic pathways in biological systems<sup>5</sup> and, in nuclear medicine, to diagnose and locate diseased sites from the differential assimilation of radioactive atoms (along with the inactive atoms) of certain elements by diseased and healthy cells of an organism.<sup>6</sup> Apart from these, radioactive isotopes are in use to estimate the wear and tear of high speed steel tools, in detecting minute leaks or cracks in huge welded structure,<sup>2</sup> to mention just a few of their numerous applications.

In the case of those elements which have variable oxidation states like sulfur and iodine, the radioactive isotopes are usually supplied commercially in the form of known oxidation states. For instance, the Bhabha Atomic Research Centre supplies isotopes of radioactive  $^{35}\text{S}$  in the form of  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$  or elemental  $\text{S}^0$ , either with or without carrier. If such a sample of  $^{35}\text{S}^{2-}$  is used by a consumer to study its interaction with a system which may change it to the  $\text{SO}_4^{2-}$  form, it is very essential that the radioactive  $\text{S}^{2-}$  solution should be absolutely free from  $\text{SO}_4^{2-}$ . However, in solutions of radioactive isotopes, particularly in high strength, radiolytic as well as non-radiolytic oxidation and reduction processes are always possible. It is, therefore, very important to investigate about the extent to which such changes occur as a function of the age of a radioactive sample which was initially prepared in a particular oxidation state.

Solutions of sulfide, on keeping for long periods, are known<sup>7</sup> to contain both  $\text{SO}_3^{2-}$  as well as  $\text{S}_2\text{O}_3^{2-}$ . This effect may get enhanced by radiolysis if the solution contains  $^{35}\text{S}$ . Some workers<sup>8</sup> have already used  $^{35}\text{S}^{2-}$  and  $^{35}\text{SO}_4^{2-}$  to dope separate silver chloride crystals. The doped crystals were then analysed chemically to estimate the extent to which  $\text{S}^{2-}$  has been converted into  $\text{SO}_4^{2-}$  in one case and  $\text{SO}_4^{2-}$  into sulfide in the other. The conclusions derived from such experiments would have no validity unless the radioactive dopants initially

present in a single oxidation state. Any appreciable change in the oxidation states of the radioisotopes of elements like Iodine, which is used internally in living systems, may have serious implications in terms of biological effects. There seems to be no reported investigations on the possible chemical transformations occurring with age in commercially supplied radioactive sulfur isotopes.

The immediate motive for carrying out this investigation originated in some unexpected results obtained by using radioactive  $S^{2-}$  as a dopant in studying some solid state reactions at the Nuclear Chemistry Laboratory at I.I.T. Kanpur. On analysis after the doping experiments, unusually large amount of  $^{35}S_2O_3^{2-}$  was observed. It proved impossible to conceive of any reasonable process by which this effect could occur and it was suspected that what was assumed to be a pure sample of  $S^{2-}$  might have contained some  $S_2O_3^{2-}$ . A chemical analysis by the carrier technique showed the presence of  $S_2O_3^{2-}$  in large amount in the radioactive sulfide solution supplied by BARC. Further chemical analysis of the so called thiosulfate fraction showed that the two sulfur atoms of the thiosulfate group did not have equal radioactivity. This pointed to the presence of other sulfur compounds, possibly polysulfides and polythionates, in the solution.

For the purpose of investigating this it was necessary to use a method which could identify the unknown sulfur compounds

in the carrier-free states. The present work reports the development of the anion-exchange technique as applied to the separation of the anionic forms of sulfur. Since the chemistry of the polythionates is very complex, and, as most of them are not available commercially, no efforts have been made to identify all the peaks in the elution spectra. It is shown here that a radioactive solution of sulfide contains a very large percentage of  $\text{SO}_4^{2-}$  and other sulfur compounds, possibly thiosulfate and other polythionates, as early as on the 10th day after the day of its preparation.



## CHAPTER 2

### EXPERIMENTAL METHOD

#### 2.1 General Considerations :

The present work is based on the detection of  $^{35}\text{S}$  in various oxidation states by its radioactivity. The concentration of radioactive  $^{35}\text{S}$  nuclide which is present to the extent of  $10^{14}$  atoms per millicurie cannot be determined by any conventional analytical method.  $^{35}\text{S}$  is a nuclide with a half life of 87 days which decays by pure beta emission to  $^{35}\text{Cl}$ . The maximum energy of the beta rays is 0.167 MeV. These "soft" beta rays are easily absorbed by air and the window material in a Geiger-Müller counter. Further it is considerably attenuated by self-absorption in the final form of the sample which is counted in a counter. These factors dictate a careful choice of the counter and corrections for self-absorption in the final chemical form of  $^{35}\text{S}$  in which it is counted. A liquid scintillation counter, a windowless gas flow counter and a thin window GM counter are the choice in decreasing order of preference.

#### 2.2 Measurement of Radioactivity :

The decay of a radioactive substance is accompanied by the emission of alpha particles, beta particles and gamma rays, either singly or in combination. Since radioactive disintegration is a unimolecular reaction of the first order, the intensity

of the emitted particles or the gamma rays is proportional to the concentration of the radioactive substance at the moment of their emission. Any device that allows a quantitative detection of the particles, or gamma rays would enable us to measure the concentration of the radioactive substance. The methods of detecting alpha and beta particles would be identical, since both of them are electrically charged, while the gamma rays require a different method of detection because it is a form of electromagnetic radiation. Since, in the present work, the radioactivity of the sample is due to the emission of pure beta particles, the general methods of detection will be described, laying emphasis on the method of measuring beta activity.

### 2.2.1 Liquid Scintillation Counting :

Nuclear radiations can interact with fluorescent or phosphorescent materials to cause photon emission and this process is known as scintillation. These light flashes are amplified in a photomultiplier tube and the photoelectrons generated in them are suitably converted into a voltage pulse. The fluorescent or phosphorescent materials are known as scintillators. Some of the well-known scintillators are NaI(Tl), anthracene and Zinc sulfide. Liquid scintillators are prepared by dissolving a suitable scintillator in an organic solvent. For example a widely used liquid scintillator consists of .

---

Napthalene - 60 g  
 2,5 - Diphenyl oxazole - 4 g  
           (PPO)  
 1,4 - Di (2-(5-phenyl oxazolyl)) benzene - 0.2 g  
           (POPOP)  
 Methanol - 100 ml  
 Ethylene glycol - 20 ml

in one litre of the solution made up by P - Dioxane,  
 which was suggested by G.A. Bray et al.<sup>10</sup> The liquid  
 scintillation counting involves dissolving the sample to be  
 counted directly in the liquid scintillator. Under these con-  
 ditions problems relating to self-absorption, attenuation of  
 particles by detector windows and the backscattering from the  
 detector are completely avoided. These advantages are parti-  
 cularly important for low-energy beta particles emitted by  
<sup>14</sup>C and <sup>35</sup>S isotopes.<sup>11</sup>

The first step in the technique involves incorporation of  
 the sample within a suitable liquid scintillator solution. A  
 common problem is that the introduction of the sample tends to  
 reduce the scintillator light output compared with the pure  
 scintillator. This phenomenon, commonly called "quenching," limits  
 the amount of sample material that can be efficiently incorpora-  
 ted within the scintillator solution. For 10 ml of the above  
 mentioned liquid scintillator 1 ml of aqueous sample solutions  
 is usually satisfactory. The quenching can be either due to

alteration of the optical properties of the solution by the sample ("color quenching") or through the interference with the energy transfer process within the scintillator itself.

After the sample has been prepared, the solution is normally loaded into a glass vial and placed in a light-tight enclosure viewed by one or more photomultiplier tubes. The noise due to photomultipliers are eliminated by coincidence counting and the thermionic emission of electrons are minimized by cooling the detector system.

Since all beta particles emitted by the sample pass through some portion of the scintillator and the great majority are fully stopped within the solution, the counting efficiency can be potentially close to 100%. For the liquid scintillator suggested by Bray et al <sup>10</sup>, the overall efficiency is 65.6% for  $^{14}\text{C}$  and 11.7% for tritium. This high efficiency for soft beta particles makes it the best choice for soft beta detection.

### 2.2.2 Detection of beta particles :

The most useful method of measuring the beta particle activity depends on the principle of multiplicative ion collection. A charged particle with a high velocity passing through a gaseous medium causes ionization of the gas molecules or atoms due to inelastic collisions with them. Further, if the gas is maintained between two electrodes with a high potential gradient between them, then the ionization phenomenon becomes enhanced due to the acceleration imparted to the initial ion-pairs

produced. As the voltage gradient is increased, the electrons, produced by the initial encounter between the incident particle and the gas atoms, themselves become sufficiently accelerated to knock out fresh electrons from the neutral gas molecules or atoms. This leads to the multiplication of the number of ions initially produced.

In practice, the cathode consists of a hollow metallic cylinder with a thin wire stretched along the central axis serving as the anode. This arrangement allows a maximum voltage gradient between the anode and the cathode for a given applied voltage. The cylinder is filled with a suitable ionizable gas and the electrode system is connected to a linear amplifier with a high gain. If the pulses are studied as a function of the applied voltage, it is found that for very low applied voltages, there is no amplification of the ionization current. As the potential is increased, amplification sets in. The pulse height at a particular voltage is proportional to the amount of initial ionization caused by the incident particle, so that it is possible to differentiate between alpha and beta particles. When the device is operated in this voltage region it is termed a proportional counter.

At higher voltages each initial ionization causes a shower of secondary ionizations, known as the "Townsend avalanche", which completely blurs out all distinction between the nature of the initial ionizing events. If the detecting device is operated in this region it is termed as Geiger counter.

.

Operation in the proportional region has many advantages, although the pulses produced are smaller than those in the Geiger region, because of the smaller applied voltage. The proportional counter has greater stability and reproducibility and the dead-time loss is of the order of a few microseconds. The voltage interval over which the count rate remains almost the same, known as the length of the plateau, is much greater than that of the Geiger counter.

### 2.2.3 Selection of counter for $^{35}\text{S}$ :

As stated earlier, the best detector would have been a liquid scintillation counter. However there are certain restrictions associated with detection by a liquid scintillation counter. A very large number of samples had to be counted during this work and would have involved the use of considerable volume of expensive liquid scintillator. Since the count rates were not very poor, windowless gas flow proportional counter was used for the detection of beta particles.

### 2.2.4 Description of the Gas Flow Proportional Counter :

The proportional counter used was the windowless  $2\pi$  geometry IL302 counter manufactured by ECIL, India. It has a manual sample changer with three sample trays. While one is in the counting chamber, the second gets preflushed by indane gas and the third awaits the next sample. The trays are situated on a rotating disc and can be rotated manually. The main

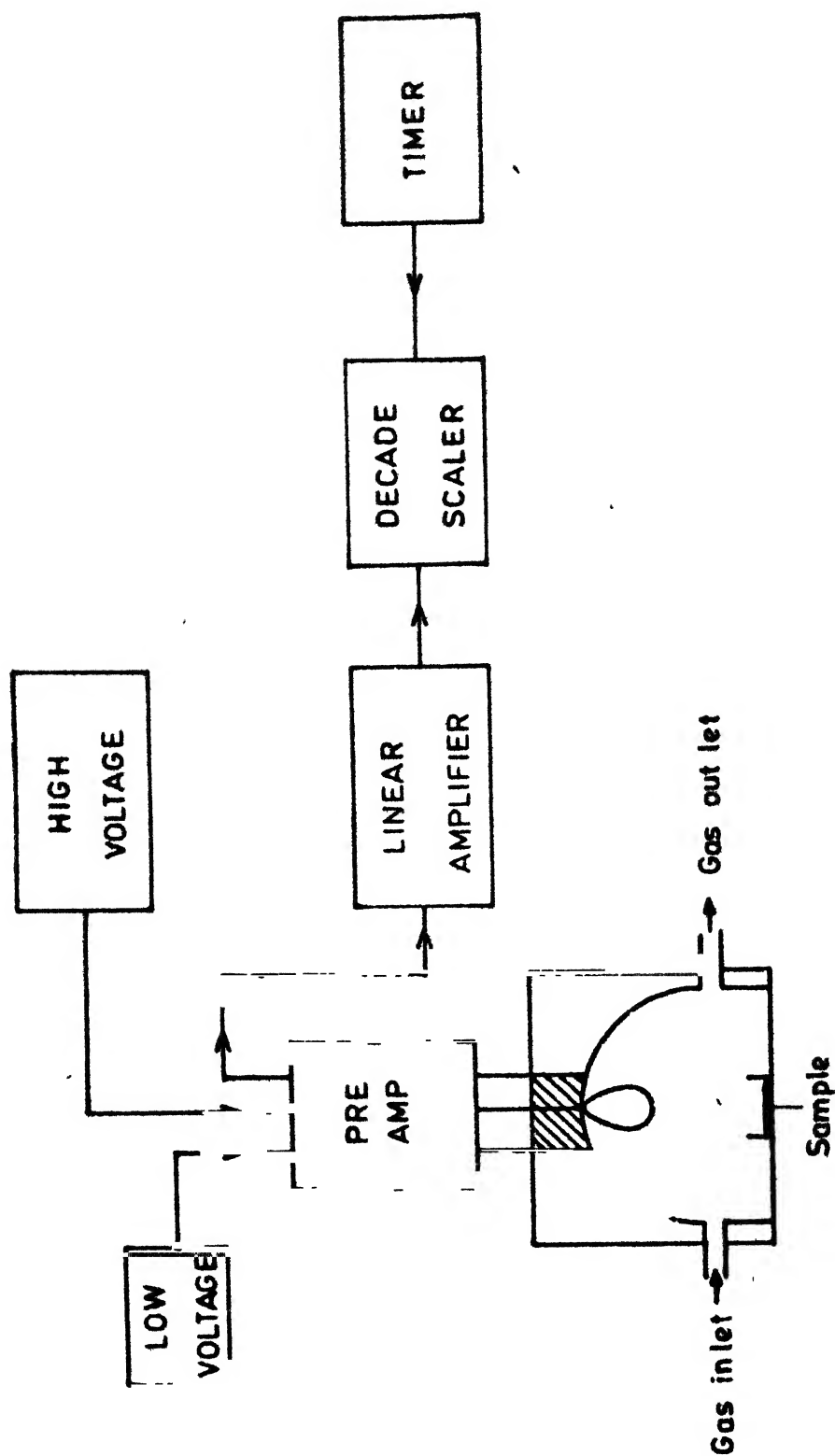


Fig. 1. Schematic diagram of the counting system.





parts of the counter are made up of stainless steel. The counting gas is indane gas supplied by the Indian Oil Corporation which is passed through a 'U' tube filled with silica gel to remove the moisture present in the gas. In order to control the gas flow rate the outgoing gas is passed through a bubbler containing liquid paraffin. The bubbling rate is adjusted by a pinch-cock so that a small positive gas pressure is always maintained inside the counting chamber. The counting chamber contains a wire anode kept at high voltage, which is the detector. This is connected to a preamplifier. The pulse from this is fed into a linear amplifier. After amplification the pulse is counted in a decade scaler which is connected with the timer. A schematic diagram of the counting system is given in Fig. 1 and the Fig. 2 shows the photograph of the counting system used in this experimental work. The gas flow proportional counter would henceforth be called the GFP counter.

#### 2.2.5 Determination of the Plateau voltage and

##### Operation of GFP counter :

For a proportional counter the pulse height is directly proportional to the operating voltage but the count rate for a particular source exhibits a plateau over a certain voltage range<sup>12</sup>. So the counter is operated in the plateau region to eliminate any change in the count rate due to voltage fluctuations. To determine the plateau region a sample of  $\text{Na}_2^{35}\text{S}$  dried in a planchet was placed on the counting tray and indane

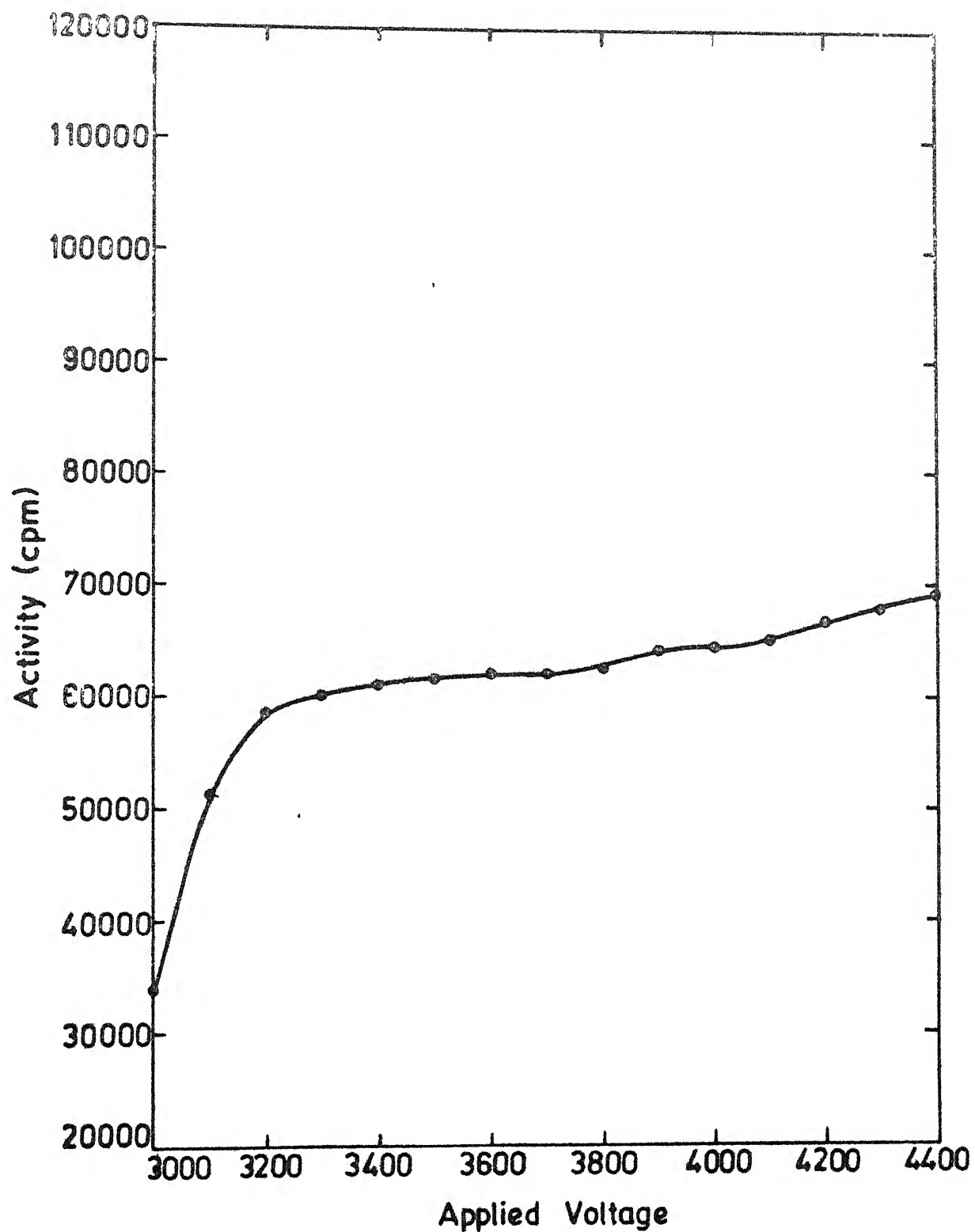


Fig. 3. Plot of count rate vs applied voltage to find the voltage plateau.

gas was bubbled through, to purge out all the air present and the high voltage was switched on. The pulse from the detector after preamplification followed by linear amplification was counted by a decade scaler. The plateau was found out by observation of count rate as a function of voltage across the detector. This is shown in Fig. 3. The voltage was varied in steps of 100 volts. The plateau was observed to be in the range of 3300 - 3800 volts. The counter was therefore operated at 3600 volts. To detect any day to day variation in counting a uranium foil was used as a reference beta particle source.

## 2.3 Separation of Sulfur Products :

### 2.3.1 Chemical method .

Since in a radioactive  $^{35}\text{S}^{2-}$  solution, the number of atoms of  $^{35}\text{S}$  present is of the order of  $10^{14}$  in a solution of 1 millicurie strength, ordinary chemical methods cannot be used to separate the different species of  $^{35}\text{S}$  present in the solution. One can, however, add appropriate inactive carriers in milligram quantities in the same oxidation state as that of the radioactive  $^{35}\text{S}$  and the separation can be performed by usual chemical procedures. Since the active and inactive atoms are chemically indistinguishable as they are in the same oxidation state, the radioactive atoms are separated along with the inactive ones. Final precipitation is done in a form which can give a uniform and coherent deposition so that it can be

counted over a long period of time.

The general scheme for chemical separation is as follows. Appropriate amounts of the inactive carriers in the form of  $S^{2-}$ ,  $SO_3^{2-}$  and  $S_2O_3^{2-}$  are added to the solution containing  $^{35}S$  in all these oxidation states. Sulfide is separated by adding a solution of  $Cd^{++}$  when  $CdS$  precipitates out. The supernatant liquid is treated with a solution of  $Ba^{++}$  when  $SO_4^{2-}$  and  $SO_3^{2-}$  together are precipitated as a mixture of  $BaSO_4$  and  $BaSO_3$ . Then the final filtrate contains  $S_2O_3^{2-}$ . The  $S_2O_3^{2-}$  is converted into  $SO_4^{2-}$  by oxidation with  $Br_2$  in  $NaOH$ . This sulfate is then precipitated as  $BaSO_4$ . The  $S^{2-}$  obtained in the form of  $CdS$  is also converted into sulfate by oxidation with  $Br_2$  in  $NaOH$  and precipitated as  $BaSO_4$ . The mixture of  $BaSO_4$  and  $BaSO_3$  is also oxidized into  $BaSO_4$  with  $Br_2$  in  $NaOH$ . Thus all the  $^{35}S$  present initially in different oxidation states are ultimately counted in the form of  $BaSO_4$ . If care is taken to add the calculated amounts of sulfide, sulfite, sulfate and thiosulfate inactive carriers so that the final theoretical yield of  $BaSO_4$  is the same and if the chemical yield is close to 100%, then the problem of correction for self-absorption and backscattering can be eliminated.

### 2.3.2 Inadequacy of chemical method :

The main drawback of the chemical precipitation method is that it assumes that there are no radioactive species in chemical states other than those of the inactive carriers added.

This method, therefore, cannot be used in case there are other chemical species present whose existence in the radioactive mixture cannot be guessed, and therefore, no corresponding inactive carrier can be added. In such cases the species having oxidation states other than that of the carrier added partly remain in solution and partly get adsorbed to variable extents on the precipitate of the known oxidised state for which carriers are added. This was found to be so in the analysis of radioactive sodium sulfide solution by Huddu Krishna and Mukherji<sup>9</sup>. It was found by them that the thiosulfate fraction contained not only thiosulfate but also some other species. When the fraction assumed to be thiosulfate was chemically split by  $\text{Ag}^+$  the two sulfur fractions were found to have unequal activities. This indicated that this fraction contained, possibly,  $^{35}\text{S}$  in other chemical forms in addition to the  $\text{S}_2\text{O}_3^{2-}$  form. This necessitated the search for some method by which one could study each species in a carrier-free state. This could be achieved only by the ion-exchange separation technique.

## 2.4 Ion-Exchange Chromatographic Technique :

### 2.4.1 Principle of Ion exchange chromatography.

Ion exchange resins are cross-linked polymers with ionic end groups like sulfonic acid ( $-\text{SO}_3\text{H}$ ) or quaternary ammonium salt end groups like  $-\text{NR}_3^+\text{OH}^-$  or  $-\text{NR}_3^+\text{Cl}^-$ . In these

resins  $H^+$ ,  $Cl^-$  and  $OH^-$  are called mobile ions because they can move through the resin but cannot come out in the absence of another ion to replace them. Their counterpart is known as fixed ions, since they are permanently linked by a covalent bond to the polymer chain which is immobile. When a solution containing ions are brought into contact with these resins, they exchange their mobile ions. When these resins are packed in a column, different types of ions present in the solution are absorbed at different heights depending upon their affinity. These absorbed ions can then be eluted with suitable eluants. Upon elution they come out at different volumes of the eluant and hence a mixture of ions can be separated as they would come out in different portions of the eluant volumes. The identification of the species can be done by comparing the elution spectra with the elution spectra of known ions. If the peaks in the spectra are well-resolved then each peak corresponds to a particular chemical species. If they are not well-resolved, they may be composite peaks representing more than one chemical species each. In that way one can identify the minimum number of chemical species in a mixture just by identifying the number of peaks even if they are not well-resolved.

#### 2.4.2 Important applications of Ion-exchange chromatography:

Ion-exchange chromatographic technique is one of the most versatile techniques used to separate new chemical species or elements in their ionic form. Most of the transuranic

elements were separated and their chemical properties were studied by the use of ion-exchange chromatography. For example Ghiorso and his co-workers<sup>14</sup> prepared Mendeleevium  $^{101}\text{Md}$  by the bombardment of  $^{253}\text{Es}$  deposited on a gold foil over an area of about  $0.05\text{ cm}^2$  by alpha particles. Mendeleevium formed was ejected out by the  $\alpha$ -particle momentum and it was collected in another gold foil. It was then dissolved in aqua regia and then passed through a Dowex-1 anion exchange column. Since gold is in the anionic form  $[\text{AuCl}_4]^-$ , it is retained by the column, while the transuranic elements came out in the solution. This was then passed through a Dowex-50 cation exchange column and separated from one another by elution with  $\alpha$ -hydroxy isobutyrate. Thus various steps in the chemical separation were carried out with less than 100 atoms. Similarly for the identification and for studying the properties of  $^{261}_{104}\text{Rf}$ , Ghiorso and his co-workers<sup>15</sup> used ion-exchange chromatographic technique. Apart from these, ion-exchange chromatographic techniques are widely used for purification of water and for the isolation of uranium from low grade ores<sup>16</sup>.

#### 2.4.3 Ion-exchange chromatography of sulfur compounds :

For the separation of sulfur compounds Iguchi<sup>17</sup> used a strongly basic anionic resin (Diaion - 5A100) in nitrate form and used different eluents like 0.1 M Sodium nitrate, 0.1 M sodium nitrate adjusted to pH 9 by ammonia, ammonium nitrate adjusted to pH 9 and 1.0 M Sodium nitrate. Bhattacharya

et al.,<sup>18</sup> used long ion-exchange columns in their study of radiosulfur-35 compounds. C.W. Owens<sup>19</sup> used Remy-2Cl in chloride form of particle size 100-200 mesh in columns of size 15 cm x 9 mm. He<sup>19</sup> used different eluants for separating different components of the mixture. To elute sulfide, a mixture of 0.04 M NaCl and ammonia adjusted to pH 10.6 was used. It was eluted in the first 300 ml. Then sulfide was eluted with a mixture of 0.04 M  $\text{NH}_4\text{NO}_3$  and 30% volume by volume of acetone and the pH was adjusted to 11 by the addition of ammonia. It was eluted in the next 185 ml. Sulfate was eluted by 100 ml of 0.2 M NaCl and the sulfate with 90 ml of 1 M  $\text{NaClO}_4$ . The flow rate used by them was 12 ml per minute.

In our studies we have used Dowex 1x8 resin of 100-200 mesh size in the chloride form. The total exchange capacity of the resin is 2.4 meq/ml on the dry basis and 1.2 meq/ml on the wet basis.

#### 2.4.4 Use of short ion-exchange chromatographic column :

The column height also plays a very important role in the separation of the components in a mixture. When the column height is increased the separation is good but a large volume of eluant is necessary<sup>20</sup>. For example when a column of 12 cm height and 0.9 cm diameter was used, sulfide was eluted between 50 ml to 220 ml of 0.05 M  $\text{NaNO}_3$ . But a smaller column gave a quicker separation if the substances were present in small quantities. It was found by us that a column of 2.5 cm in height and 0.9 cm in diameter was



giving fairly well separated peaks for sulfide, sulfate and thio-sulfate. In this experiment 1.4 ml fractions of eluant from the column were collected on plastic planchets and dried in an air oven at 60°C for three hours.

Each was then counted in a GMP counter. If longer columns were used the total time taken for a single experiment would have been 30 hours. The use of small column of the above mentioned height reduced the total time to about 6 hours including the sample preparation and counting.

#### 2.4.5 Preparation of the Ion-exchange column :

A schematic diagram of the set up of the ion-exchange column is shown in Figure 4. The ion-exchange column used was made up of a glass cylinder of inner diameter 0.9 cm and a height of 10 cm. The top portion of the column was fitted with a B-19 jacket so that a reservoir with a B-19 cone or a cylindrical column for increasing the column height of the eluant could be fitted easily. The bottom of the column was fitted with a stop-cock and a small portion of the column was fitted with glass wool.

A slurry of Dowex 1x8 resin in chloride form of mesh size 100-200 was made in water and was soaked for one hour so that there would be no further swelling of the resin while in the column. Then the slurry of Dowex resin was poured into the column containing some water. In this way formation of air

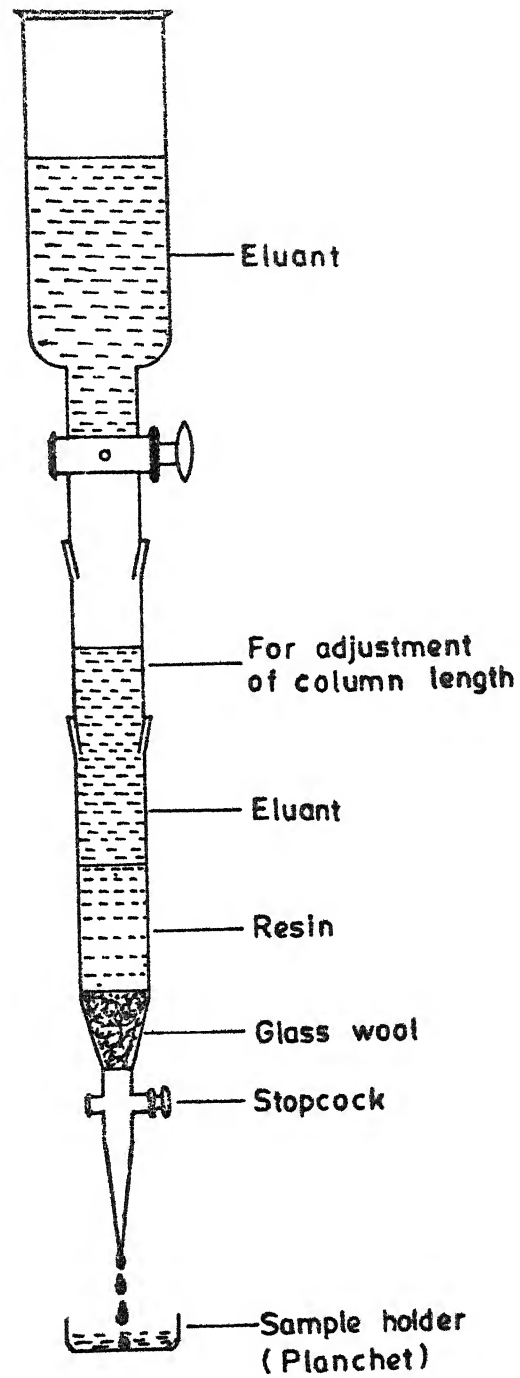


Fig. 4. Schematic diagram of ion-exchange column.

bubble in the column was avoided and the resin was allowed to settle under its own weight. After filling the column with the resin upto the required height, water was drained out by opening the stop-cock.

Before an operation the resin was washed thoroughly with distilled water to remove any excess chloride present in the resin and the washings were tested for the presence of chloride with a solution of  $\text{Ag}^+$ .

#### 2.4.6 Calibration of the column :

##### 2.4.6.1 Determination of the elution regions for chloride, sulfite, sulfate and thiosulfate .

0.3 ml of 0.02 M solution of the appropriate anion (i.e.,  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  or  $\text{S}_2\text{O}_3^{2-}$ ) was taken by a 1 ml pipette and placed at the top of separate anion exchange columns (Dowex 1x8). The column was then filled with the eluant (0.05 M  $\text{NaNO}_3$ ) to the necessary height (predetermined with distilled water) to give a flow rate of 1.5 ml per minute. The reservoir containing eluant was then attached to the column so as to maintain a constant height of the eluant in the column (See Fig. 4). 1 ml fractions of the eluant from the column were then collected and the appropriate chemical reagent was added to detect the proper anion in each successive fraction as follows.

Sulfide :

Each eluant fraction was treated with a solution of  $\text{Cd}^{++}$ . Presence of  $\text{S}^{2-}$  was shown by the yellow opalescence due to  $\text{CdS}$ .

Sulfite :

Each eluant fraction was treated with  $\text{Ba}^{2+}$ . White turbidity due to  $\text{BaSO}_3$  which was vanishing by the addition of conc.  $\text{HCl}$ , indicated the presence of sulfite.

Sulfate :

Each eluant fraction was treated with  $\text{Ba}^{2+}$ . A white turbidity due to  $\text{BaSO}_4$  which is insoluble in conc.  $\text{HCl}$  indicated the presence of  $\text{SO}_4^{2-}$ .

Thiosulfate :

Each fraction was treated with  $\text{Ag}^+$ .  $\text{Ag}^+$  has the property of breaking up  $\text{S}_2\text{O}_3^{2-}$  into  $\text{Ag}_2\text{S}$  (insoluble) and  $\text{Ag}_2\text{SO}_4$  (soluble). Since  $\text{Ag}_2\text{S}$  is black, the presence of  $\text{S}_2\text{O}_3^{2-}$  is easily detected.

The purpose of these experiments were to find out the region of the eluant volume in which a particular anion is eluted. The earliest volume at which a fraction indicated the presence of a particular anion and the final volume at which a fraction ceased to indicate the presence of the particular anion were noted. The volume between the appearance and disappearance of a particular

anion is the elution region for the particular anion. Their elution regions are shown in Table 2.1.

#### 2.4.6.2 Determination of the elution curve for sulfite with radioactive $^{35}\text{SO}_4^{2-}$ :

3  $\mu\text{l}$  of a radioactive  $^{35}\text{SO}_4^{2-}$  solution (from BARC, Bombay) was taken out by a microsyringe, diluted to 1 ml with distilled water. 0.3 ml of this was added to the top of a column of anion exchange resin (Dowex 1x8) and the same procedure as described above was followed. Successive fractions of eluant, 1.4 ml each, were collected, dried on planchets at  $60^\circ\text{C}$  and then counted in GMP counter. From the plot of activity per fraction against the volume of the eluant at which the fraction was collected, the elution region and the elution curve obtained for  $\text{SO}_4^{2-}$  is shown in Figure 5. The peak position at 33 ml coincides well with the mid-point of the elution region determined with inactive  $\text{SO}_4^{2-}$ .

#### 2.4.7 Ion-exchange Chromatographic Analysis of radioactive $\text{S}^{2-}$ solution :

The sample of radioactive  $\text{S}^{2-}$  was supplied by BARC, Bombay. It was in the form of a solution of 5 milli curies of radioactive  $^{35}\text{S}^{2-}$  in 4 ml of solution containing approximately 25 mg of inactive  $\text{Na}_2\text{S}$  as carrier. The sample was contained in a glass vial with a sealed rubber cap. Required amounts of sulfide solution were withdrawn as and when required

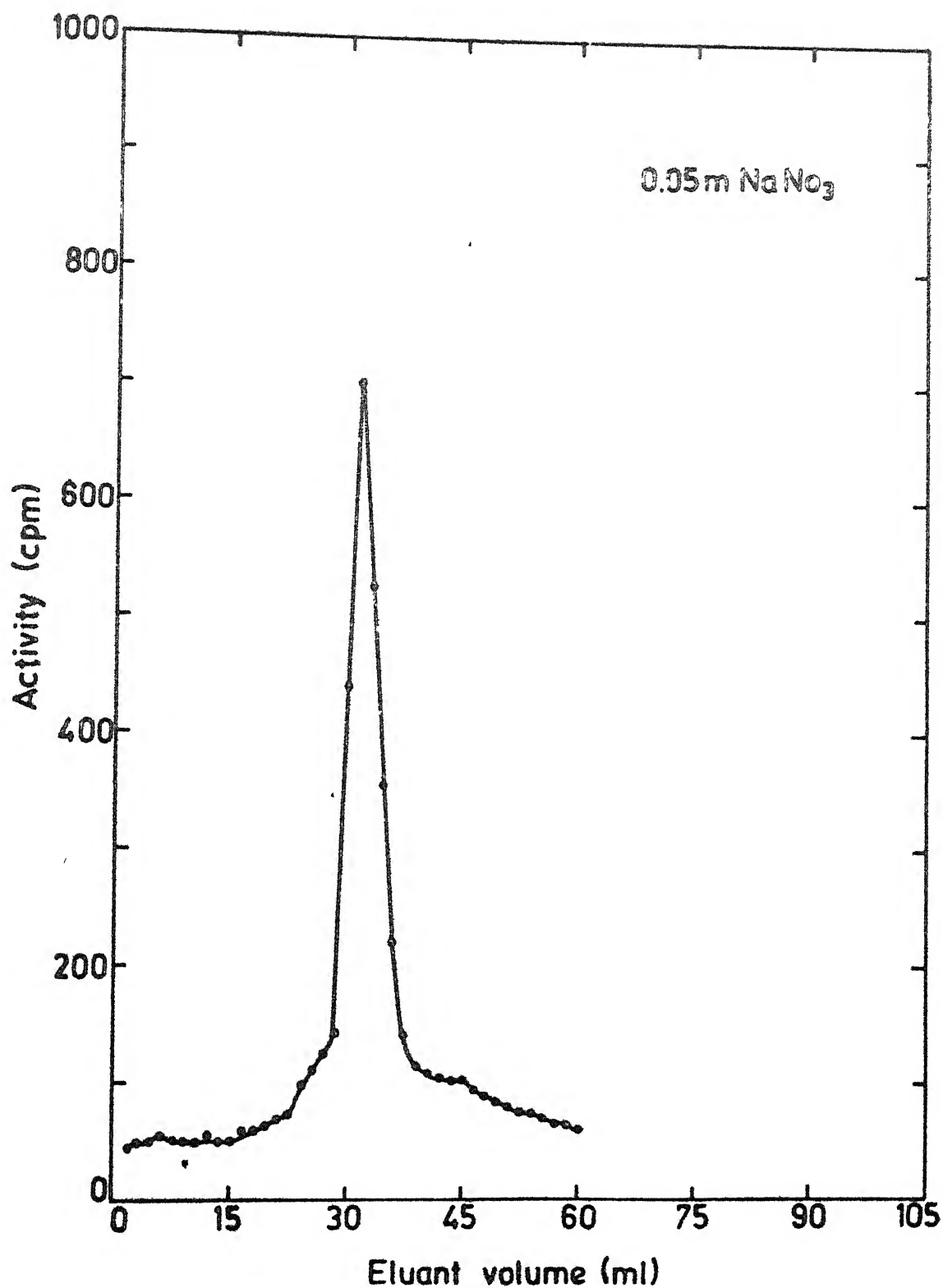


Fig. 5. Plot of the activity in 1.4 ml fraction of the eluant against the eluant volume for known  $^{35}\text{SO}_4^{2-}$ .

by means of a microsyringe. The sample was always stored inside an aluminium can, away from heat and light.

In most of the analysis 5  $\mu$ l of the sample was withdrawn and passed through the ion-exchange column. In some of the experiments 5  $\mu$ l of the sample was diluted to 1 ml of distilled water. 0.1 ml of this solution was then passed through the ion-exchange column. The column was then eluted with 0.05 M  $\text{HNO}_3$  in the same way as mentioned in the section under calibration. In some cases the column was washed with water to see if any activity was coming down out of the column. Successive fractions of eluant containing 1.4 ml were collected on circular planchets. These planchets 2.5 cm in diameter, 3.0 mm in height and about 1 mm in thickness, were made of plastic. Each fraction was evaporated to dryness at 60°C in an air oven and the activity was counted in a Gas Flow Proportional counter (GFP counter). Each ion exchange chromatographic analysis required the collection, preparation and counting of about 100 fractions. Since equal volumes of the same 0.05 M  $\text{HNO}_3$  solution was evaporated in each collected fraction the self-absorption and other counting-corrections are also identical and no relative corrections are needed either to obtain the activity distribution as a function of the eluant volume or for intercomparison of the amounts of different anions from the total activity under each curve.

In some cases, after elution with a certain volume of 0.05 M  $\text{NaNO}_3$ , elution was carried out with other higher concentrations of  $\text{NaNO}_3$ . In these cases, relative corrections were needed for the different relative amounts of  $\text{NaNO}_3$  present in 1.4 ml of the solutions of  $\text{NaNO}_3$  of different concentrations. The corrections were made as follows: 5  $\mu\text{l}$  of the radioactive  $^{35}\text{S}^{2-}$  solution was diluted to 10 ml with distilled water. Aliquots of 0.1 ml of this dilute solution was taken in planchet containing 1 ml of 0.05 M  $\text{NaNO}_3$ . These were evaporated to dryness and counted in duplicate. Similarly the same aliquot of radioactive solution was taken in planchets containing 1 ml of 0.1 M  $\text{NaNO}_3$  and 0.33 M  $\text{NaNO}_3$  solution each. These were dried and counted in duplicates. Because of the higher self-absorption, where the sample contains more of the  $\text{NaNO}_3$ , the actual count would be less than in the sample containing less of  $\text{NaNO}_3$ . Since the same quantity of  $^{35}\text{S}$  is present in all of them, the correction factor is the ratio of the observed activities in the two samples. Table 2.2 shows the correction factor with respect to 0.05 M  $\text{NaNO}_3$ .

Each such chromatographic analysis was done with an aliquot of the radioactive  $\text{S}^{2-}$  solution at different periods of time. The elution curves obtained with the samples analyzed at different times gave an idea of the type of interactions inside the solution between the species present as a function of the age of the sample. The actual results and discussions on their significance are presented in the next chapter.



TABLE 2.1

Elution regions with 0.05 M  $\text{NaNO}_3$  in terms of eluant volume.

Species	Elution region
$\text{S}^{2-}$	0 ml - 22 ml
$\text{SO}_3^{2-}$	15 ml - 30 ml
$\text{SO}_4^{2-}$	22 ml - 43 ml
$\text{S}_2\text{O}_3^{2-}$	61 ml - 133 ml

TABLE 2.2

Correction factor for self-absorption with respect to 0.05 M  $\text{NaNO}_3$

Conc. of eluant ( $\text{NaNO}_3$ )	Average activity (cpm)	Multiplication factor v.r.t. 0.05 M $\text{NaNO}_3$
0.05 M	1646.5	1
0.1 M	1129.4	1.46
0.33 M	907.95	1.81

## CHAPTER 3

### RESULTS AND DISCUSSION

#### 3.1 Results .

In this section are first presented the results of the chemical analysis of a radioactive sulfide sample by inactive carrier technique (Section 2.3) by Muddavarishna and Mukherji<sup>9</sup>.

If it is assumed that the solution contains only  $S^{2-}$ ,  $SO_3^{2-}$ ,  $SO_4^{2-}$  and  $S_2O_3^{2-}$ , then the addition of  $Ag^+$  to the filtrate after removal of  $S^{2-}$  as  $CdS$ ,  $SO_3^{2-}$  and  $BaSO_3$ ,  $SO_4^{2-}$  as  $BaSO_4$ , should cause the activity in the original  $S_2O_3^{2-}$  to appear in equal amounts in the  $Ag_2S$  and  $Ag_2SO_4$  fractions. The last two columns of Table 3.1 shows that the activity of the two fractions (i.e.,  $Ag_2S$  and  $Ag_2SO_4$ ) obtained from the assumed  $S_2O_3^{2-}$  in the filtrate are not the same. This indicated possibly that sulfur compounds other than the ones considered are also present in the solution.

The results of the present analysis are given in the form of elution curves of samples removed from the radioactive  $S^{2-}$  solution at different time periods. Each curve shown in Fig. 6-14 represents a plot of the activity in successive 1.4 ml fractions of the eluant against the volume of the eluant at which the fractions are collected.

TABLE 3.1

Chemical separation data of  $\text{Fe}_2^{3+}$  solution

Age of the sample	$\text{S}^{2-}$	$\text{SO}_3^{2-} + \text{SO}_4^{2-}$	$\text{S}_2\text{O}_3^{2-}$	$\text{SO}_4^{2-}$ from $\text{S}_2\text{O}_3^{2-}$ %	$\text{S}^{2-}$ from $\text{S}_2\text{O}_3^{2-}$ %
	%	%	%	%	%
6 months	21.7	26.2	52.0	-	-
	21.4	24.5	54.1	-	-
15 months	2.30	77.7	-	14.4	5.5
	2.2	75.9	21.8	-	-

Fig. 6 is the earliest sample that could be analyzed (7 day old). It exhibits two clear peaks at 16 ml and 33 ml eluant volume. From the previous calibration (Section 2.4.6) the first peak on the left seems to be a mixture of  $S^{2-}$  and  $SO_3^{2-}$  and the second peak is mainly due to  $SO_4^{2-}$ . Because of a misunderstanding at that time regarding the elution regions of  $S_2O_3^{2-}$ , elution beyond the volume of 60 ml was not undertaken.

Figure 7 shows a similar analysis of 10 day old  $S^{2-}$  solution. Here the first peak on the left seems to be the sulfide peak, which makes one suspect that the left hand side peak in Fig. 6 might have been due to a mixture of  $S^{2-}$  and  $SO_3^{2-}$ . The second peak is possibly that of  $SO_3^{2-}$  and the third and the most prominent peak is that of  $SO_4^{2-}$ . This is confirmed by the same value of the full width at half maximum for the two curves peaking at 33 ml in Figures 6 and 7. Elution pattern beyond the volume of 45 ml seems to show the presence of at least 3 to 4 sulfur compounds. Since the region 61 ml - 123 ml represents the volume in which  $S_2O_3^{2-}$  is eluted, it is suspected that  $S_2O_3^{2-}$  and other polythionic acids are present in the solution.

In order to have a broad idea about the nature of the compounds present, an aliquot of the sample of radioactive  $S^{2-}$  taken on the 10th day was treated with 1 ml of conc. HCl in a test tube, evaporated to dryness and was extracted with water and subjected to ion-exchange separation. The acid is expected to cause  $S^{2-}$ ,  $SO_3^{2-}$  and thiosulfate as well as polythionate

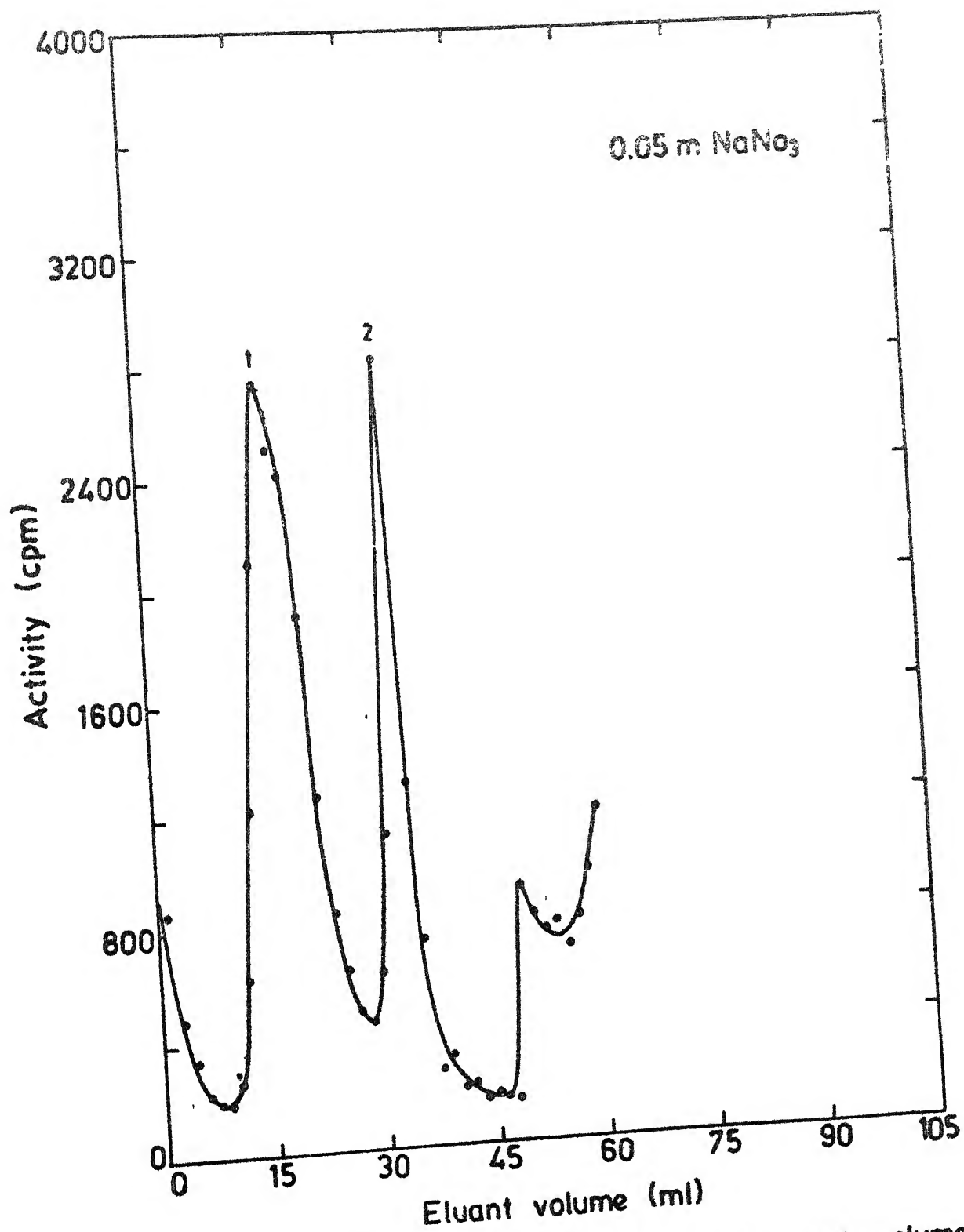


Fig. 6. Plot of eluted activity per 1.4 ml of eluant volume for a 7-day old sample of radioactive sulphide.

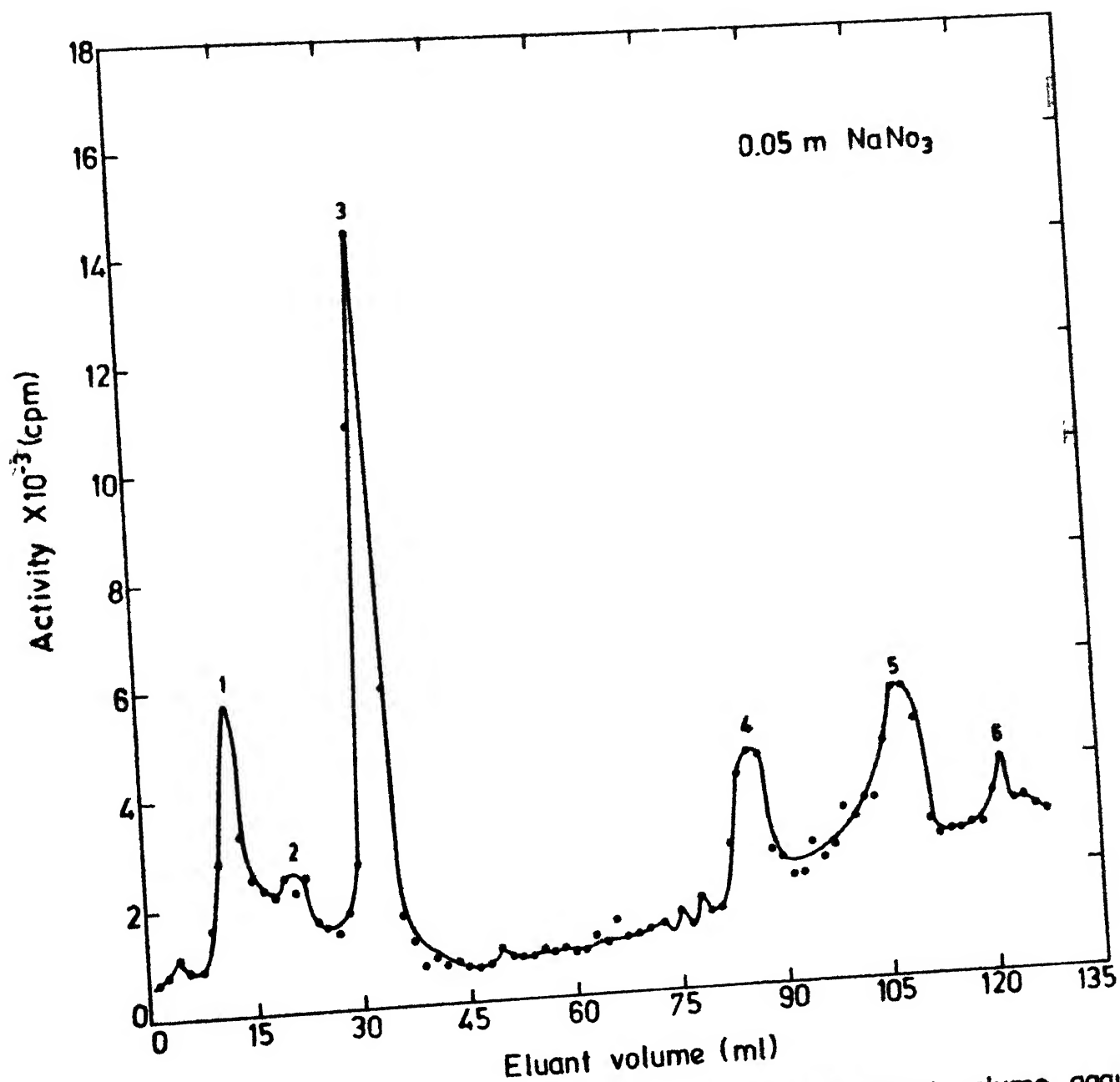


Fig. 7. Plot of eluted activity per 14 ml of the eluant volume against the eluant volume for a 10-day old sample of radioactive sulphide.

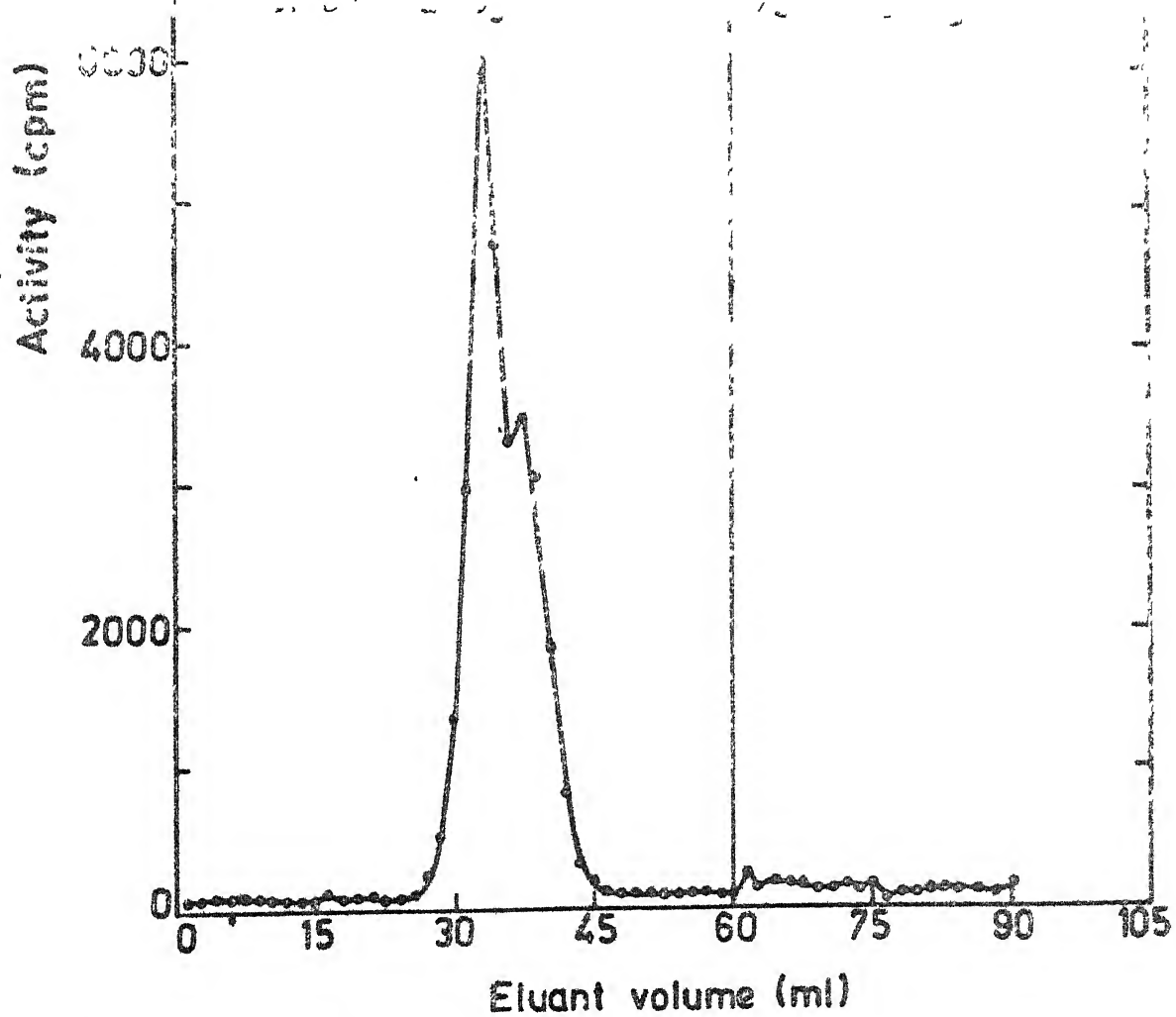


Fig. 8. Plot of eluted activity per 1.4 ml of eluant against eluant volume for an acid treated 10 day old sample of radio-active sulphide.

peaks to vanish.  $\text{SO}_3^{2-}$  yields volatile  $\text{SO}_2$ ,  $\text{S}^{2-}$  would evaporate as  $\text{H}_2\text{S}$ , thiosulfates and polythionates would yield first S, and a mixture of  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$ . Since  $\text{SO}_2$  and  $\text{H}_2\text{S}$  would go away and elemental S would precipitate out (or would be adsorbed on the column later) and only  $\text{SO}_4^{2-}$  would be seen in the eluant. Figure 8 shows the elution spectrum for the 10 - day old acid treated sample. A comparison between Fig. 7 and Fig. 8 shows that all the peaks for  $\text{S}^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  and suspected thionic acids have disappeared on acid treatment as expected. To ensure that no activity due to  $\text{S}_2\text{O}_3^{2-}$  and possible thionic acids is missed, elution of the column in the case of the acid treated sample was continued with 0.05 M  $\text{NaNO}_3$  upto a volume of 60 ml and then further elution was done with 0.33 M  $\text{NaNO}_3$ . The peak of the remaining prominent curve in Fig. 8 corresponds with that of  $\text{SO}_4^{2-}$ . However there is a small kink in this curve which is somewhat difficult to explain.

Figure 9 shows the elution spectrum of a 15 - day old sample. Some activity appears in the water used to wash the sample after it was placed on the column. Peak number 2 appears to be due to  $\text{S}^{2-}$  and peak number 3 due to  $\text{SO}_4^{2-}$ . The kink observed in the acid treated sample in Figure 8 seems more prominent now and possibly represents a new compound whose activity is growing with time and which is stable towards acids. After using 0.05 M  $\text{NaNO}_3$  upto a volume of 50 ml, 0.1 M  $\text{NaNO}_3$  was used as the eluant to have a broad view of the  $\text{S}_2\text{O}_3^{2-}$  region. Several small peaks



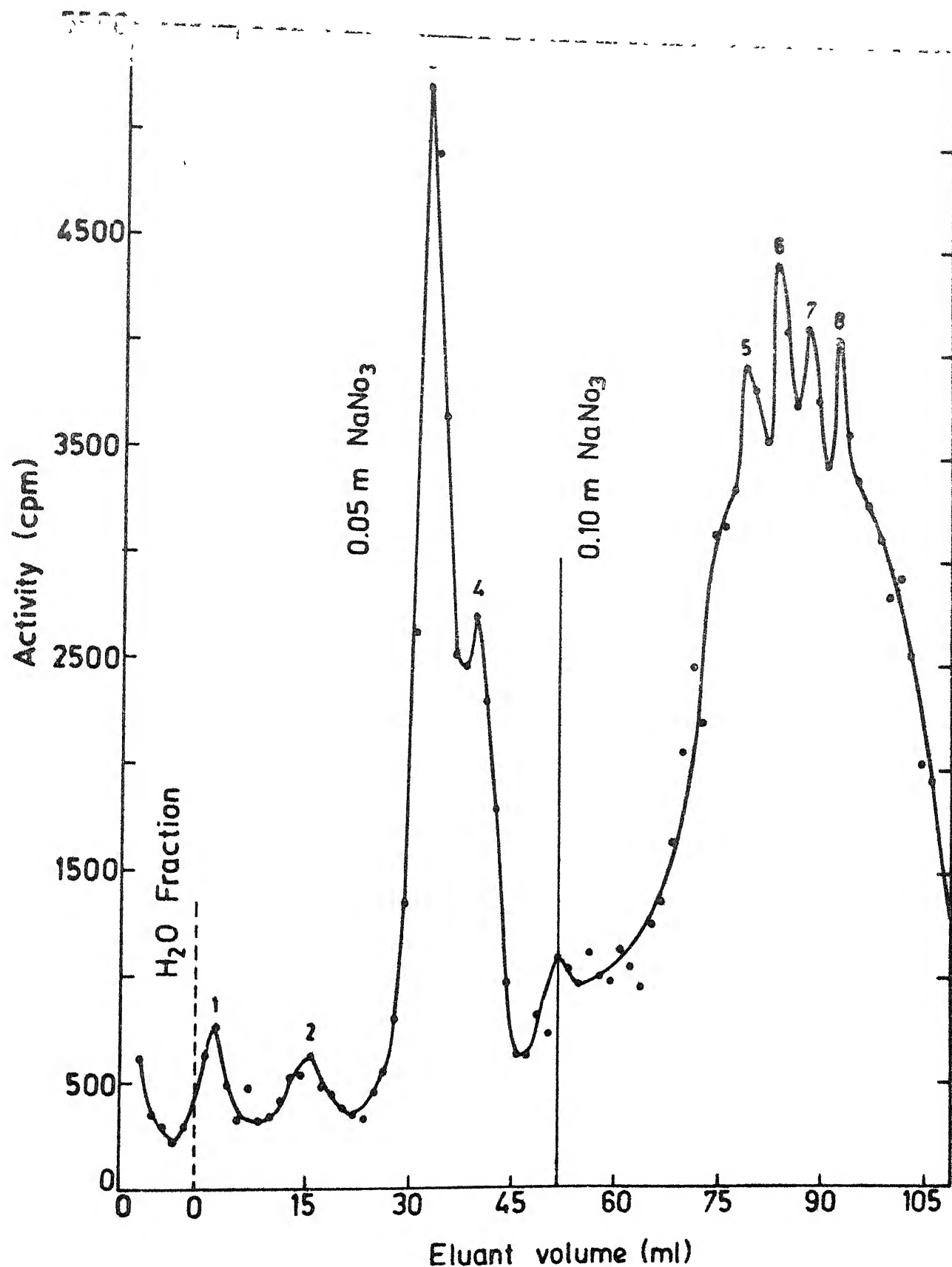


Fig. 9. Plot of eluted activity per 1.4 ml of eluant volume against the eluant volume for a 15-day old sample of radioactive sulphide.

(5, 6, 7 and 8) indicate a large number of compounds, possibly polythionates, which are growing in the solution with time. This trend continues in the 17 - day old sample in which the  $S^{2-}$  and  $SO_4^{2-}$  peaks are still prominent but no longer well-resolved, the kink on the  $SO_4^{2-}$  curve has shaped itself into another peak and the total activity in the thiosulfate and thionate is increasing (Fig. 10).

Figure 11 shows the spectrum of a 13 - day old sample, which was diluted and air-exposed for 4 days. The only broad and prominent peak seen appears to be due to a mixture of  $SO_3^{2-}$  and  $SO_4^{2-}$ . Thionates and  $S^{2-}$  are undergoing air oxidation to yield  $SO_3^{2-}$  and  $SO_4^{2-}$ . Since the peaks on the right hand side seen in the 10 - day, 15 - day and 17 - day old samples (Fig. 7, 9 and 10) are not visible in Fig. 11 this conclusion is possibly a reasonable one.

Figures 12 and 13 show respectively the elution spectra for a 79 - day old and 113 - day old sample respectively. In Fig. 12 peak numbers 3 and 4 may be due to a mixture of  $SO_3^{2-}$  and  $SO_4^{2-}$  and the cluster of curves on the right indicates a number of unresolved peaks corresponding to unknown products, possibly polythionates. Fig. 13 shows the clear  $S^{2-}$  peak (peak no. 2) and a single peak for  $SO_4^{2-}$  and a number of peaks in and beyond the  $S_2O_3^{2-}$  region on the right hand side corresponding to complex polythionates.

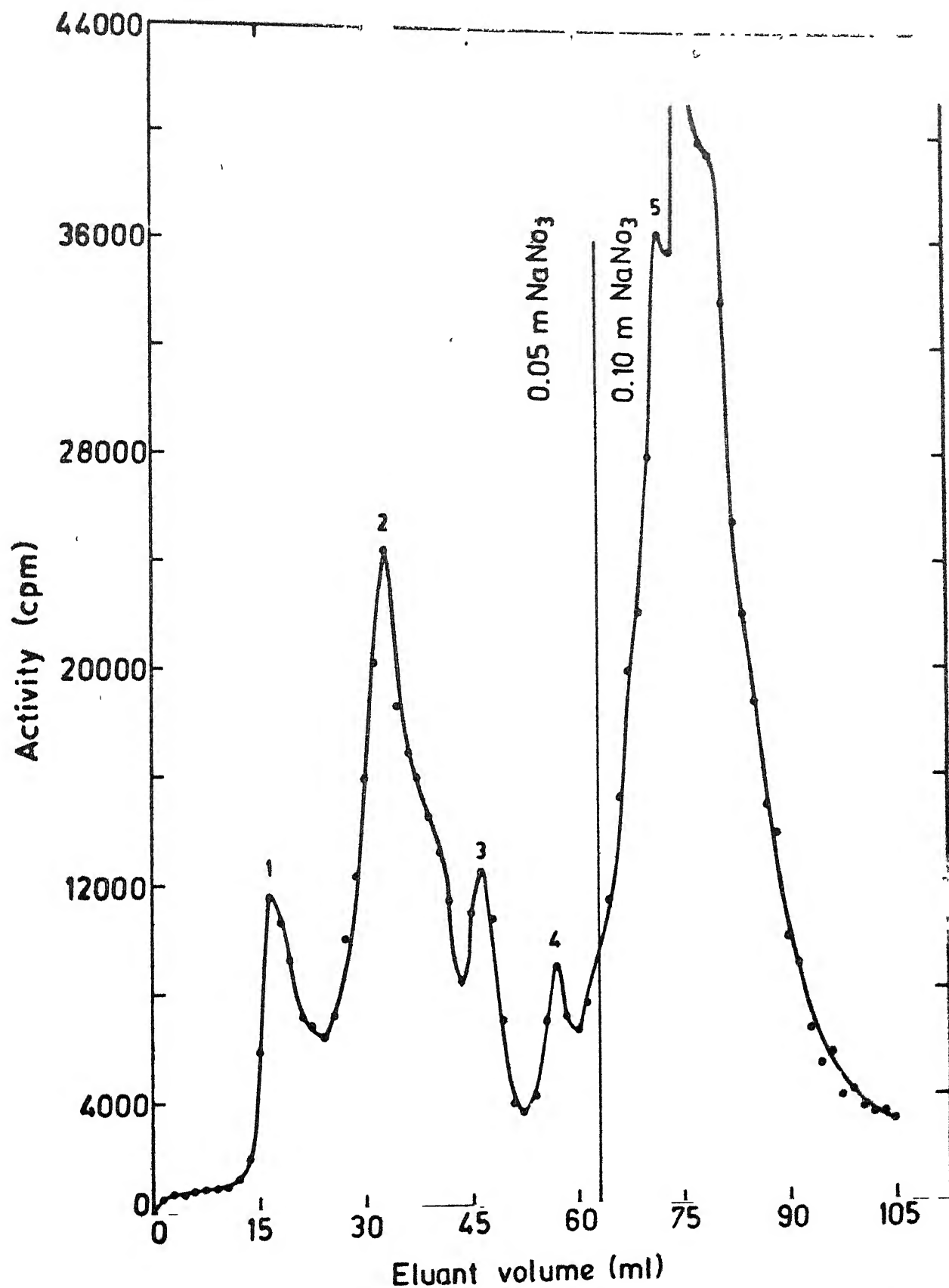


Fig. 10. Plot of eluted activity per 1.4 ml of eluant volume against the eluant volume for a 17-day old sample of radioactive sulphide.

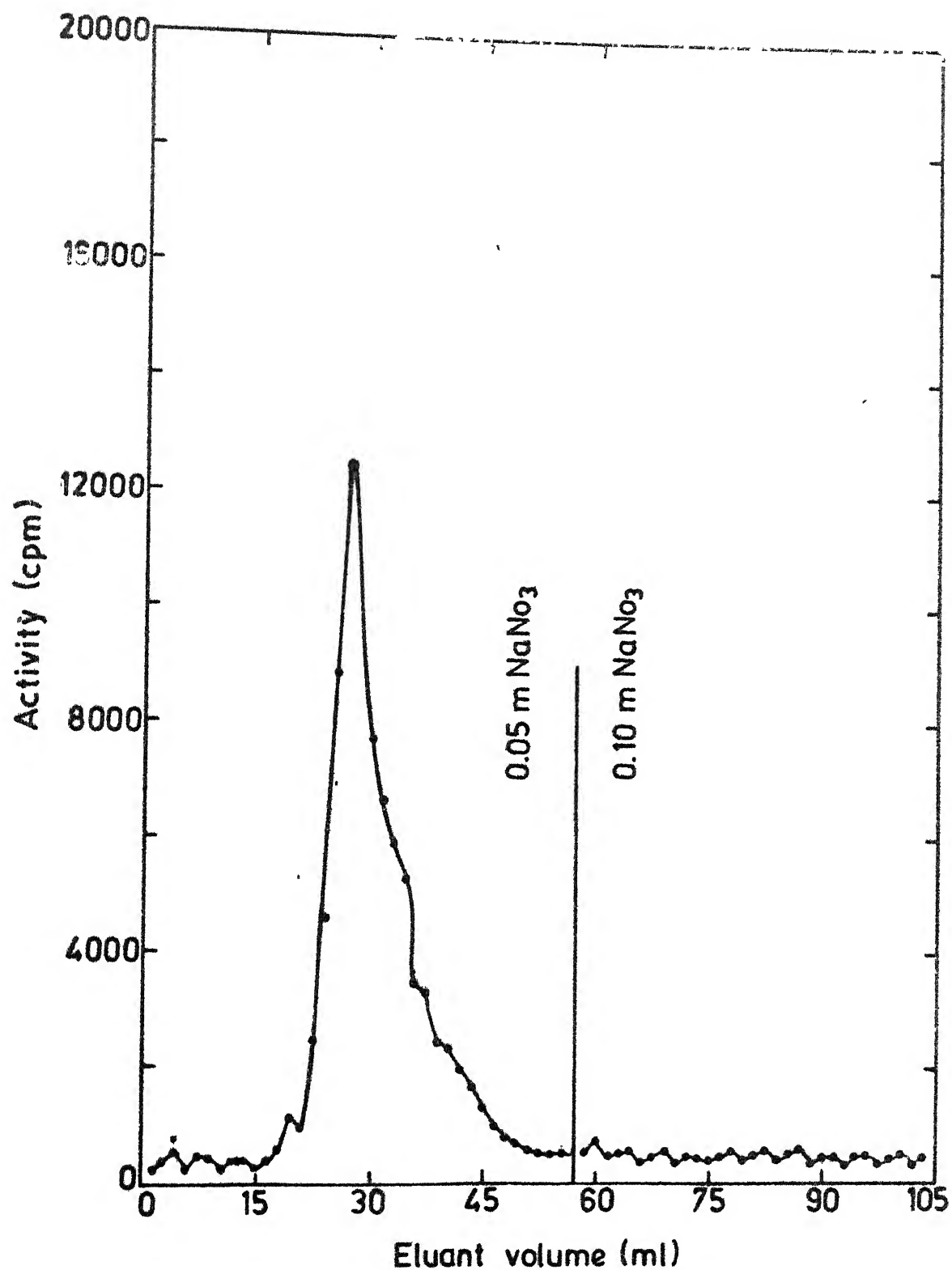


Fig. 11. Plot of eluted activity per 1.4 ml of eluant volume against the eluant volume for a air exposed diluted sample. Diluted on 13<sup>th</sup> day and analysed on 17<sup>th</sup> day.

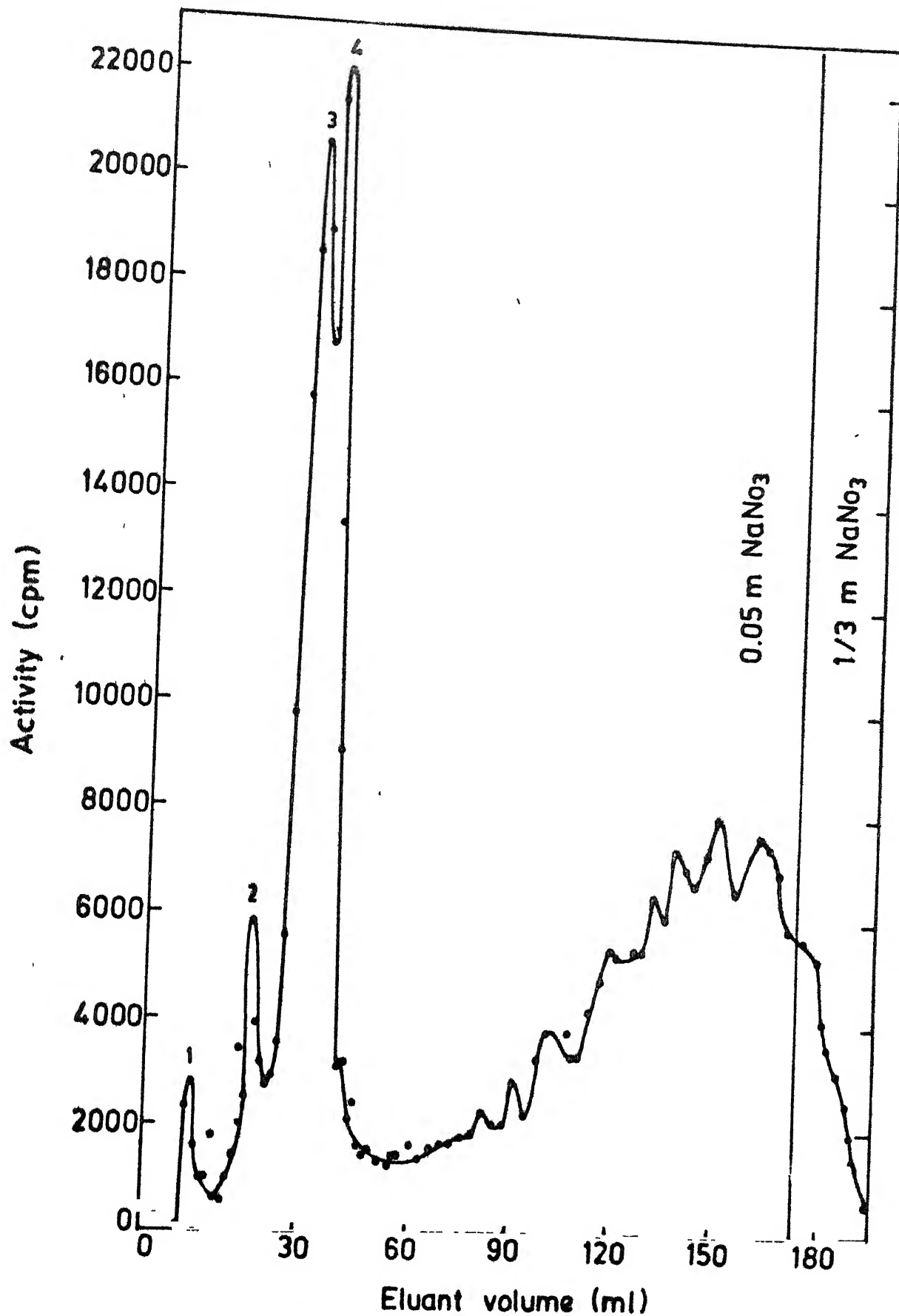


Fig. 12. Plot of eluted activity per 1.4 ml of eluant volume against the eluant volume for a 79 day old sample.

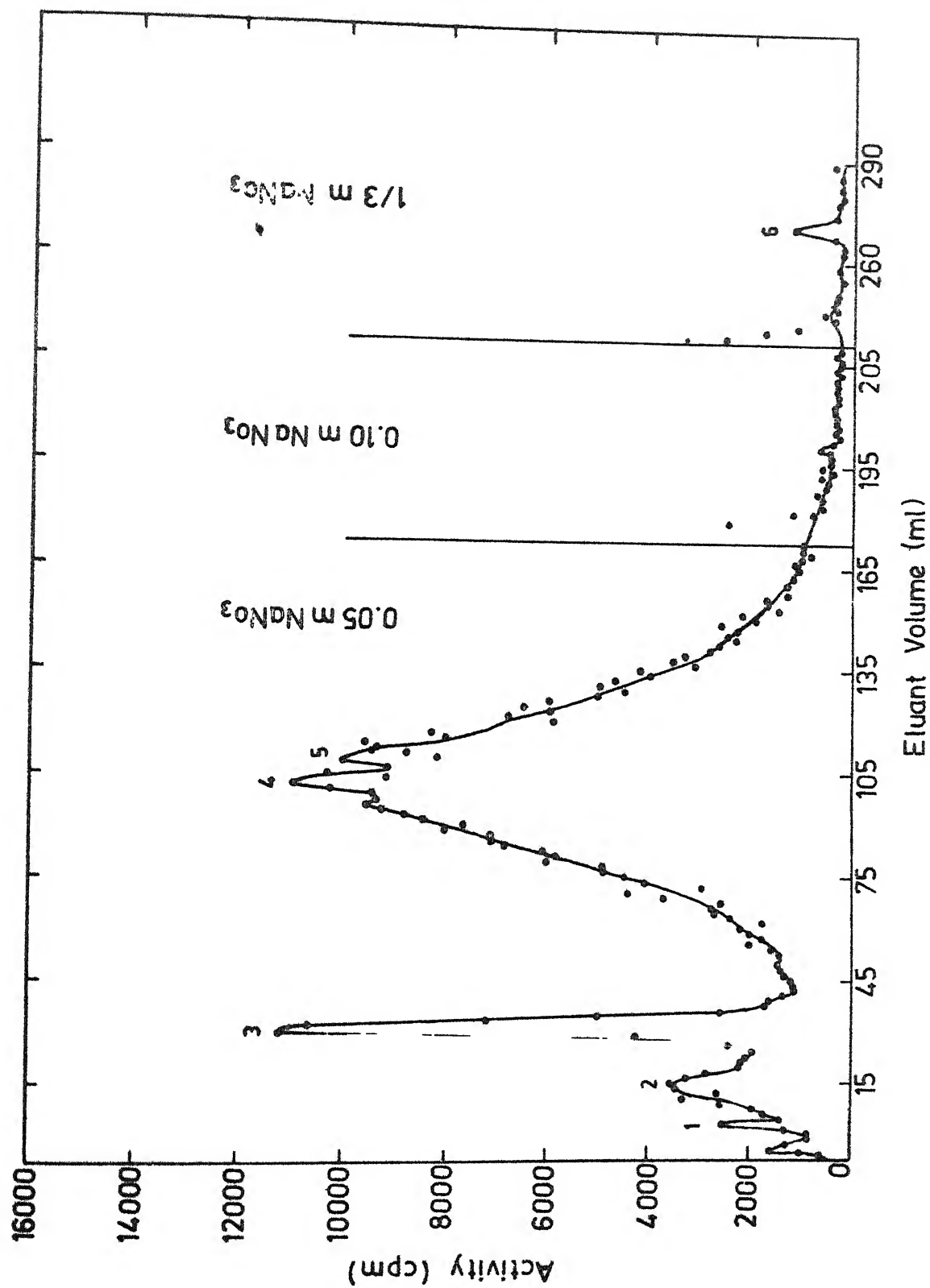


Fig. 13. Plot of eluted activity per 14 ml of eluant volume against the eluant volume for a 113 day old sample.

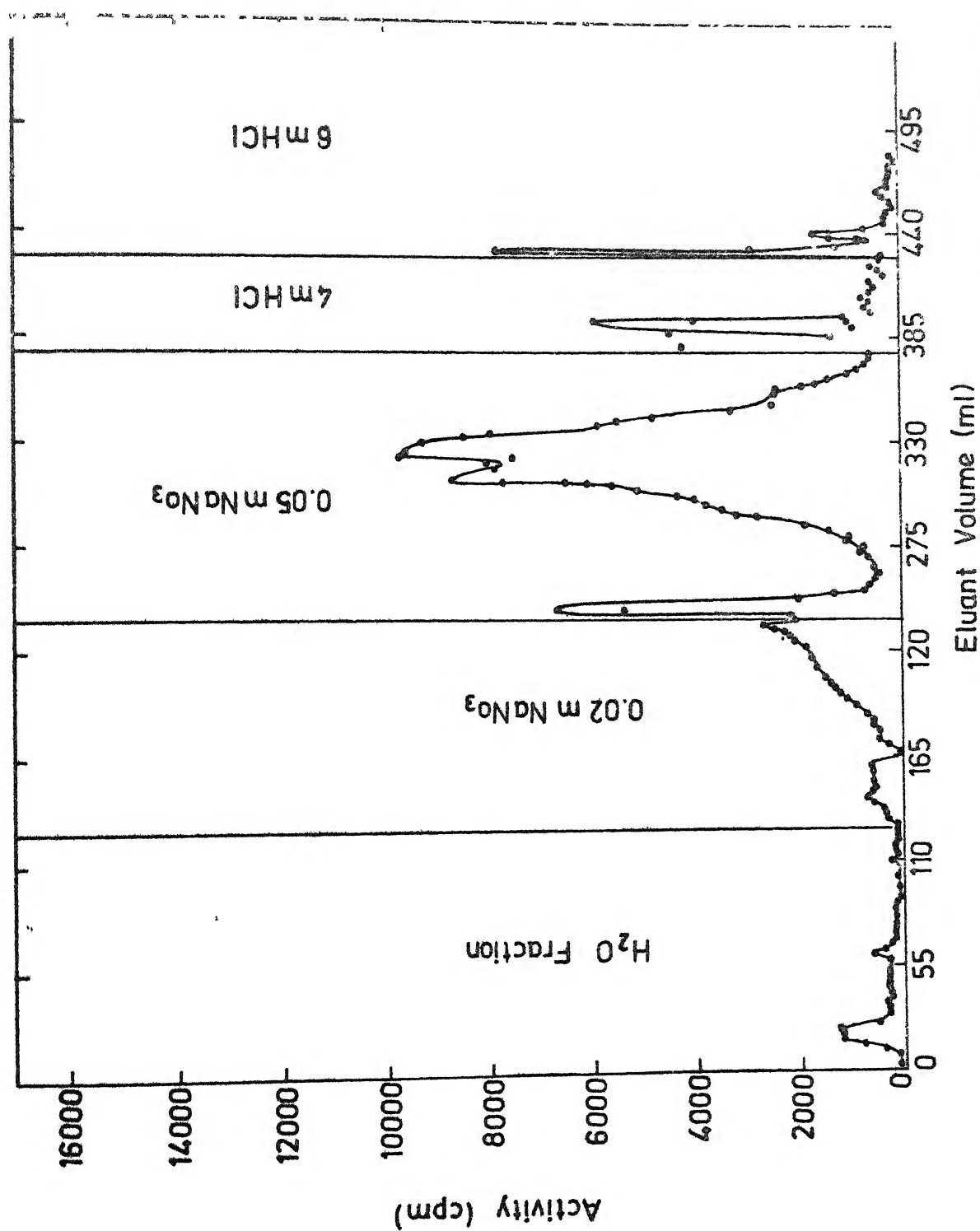


Fig. 14. Plot of eluted activity per 1.4 ml of eluant volume against eluant volume for a 115 day old sample.

TABLE 2.2

Percentages of activities in different electron regions upon ageing

Age of the $^{35}\text{S}^{2-}$ sample Number of days	Water fraction activity %	$\text{S}^{2-}$ region activity %	$\text{SO}_4^{2-} + \text{SO}_3^{2-}$ region activity %	$\text{S}_2\text{O}_3^{2-}$ region activity %
7	-	70.56	29.43	-
10	-	18.1	21.05	60.84
15	1.41	5.29	24.21	69.09
17	-	7.50	27.28	65.14
79	1.02	3.61	24.8	70.55
113	0.94	7.48	8.88	82.7



TABLE 3.3

Relative percentages of the activities in  
the  $S^{2-}$  region and in the  $SO_3^{2-} + SO_4^{2-}$  region

Age of the $^{35}S^{2-}$ sample No. of days	$S^{2-}$ region activity %	$SO_4^{2-} + SO_3^{2-}$ region activity %
7	70.56	29.43
10	46.23	53.77
15	17.94	82.06
17	21.75	78.25
79	12.68	87.32
113	45.75	54.30

Figure 14 shows the elution spectra of the sulfide sample, 115 days of its preparation, with water, 0.02 M  $\text{NaNO}_3$ , 0.05 M  $\text{NaNO}_3$ , 4 M  $\text{HCl}$ , and 6 M  $\text{HCl}$ . The column retains considerable activity which cannot be eluted even by 6 M  $\text{HCl}$ .

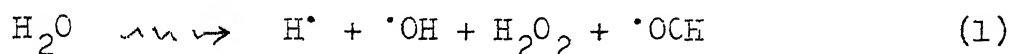
### 3.2 Discussion :

From an inspection of Figures 6-13 it seems clear that the radioactive  $\text{S}^{2-}$  solution, after 7 days of its preparation, contains considerable amount of  $\text{SO}_4^{2-}$ . Further, with age, a large number of other sulfur products also appear in the solution. Since most of the thionates are commercially not available and quite difficult to prepare in pure states, identification of all the peaks seen in the elution spectra was not possible within a limited period of time. Table 3.2 shows the approximate compositions of the solutions of different age in terms of  $\text{S}^{2-}$  fraction,  $\text{SO}_3^{2-}$  and  $\text{SO}_4^{2-}$  fraction and  $\text{S}_2\text{O}_3^{2-}$  fraction.  $\text{S}^{2-}$  fraction activity comprises the total activity computed in the region where  $\text{S}^{2-}$  should appear (9 - 22 ml). Similarly  $(\text{SO}_3^{2-} + \text{SO}_4^{2-})$  activity is the activity under the  $(\text{SO}_4^{2-} + \text{SO}_3^{2-})$  peak. The total activity in the volume of eluant beyond 61 ml is designated as the  $\text{S}_2\text{O}_3^{2-}$  fraction, which actually may consists of  $\text{S}_2\text{O}_3^{2-}$  and other polythionates and polysulfides. These relative amounts are shown in the Table 3.2. Table 3.3 shows the relative amounts of  $\text{S}^{2-}$  and  $(\text{SO}_3^{2-} + \text{SO}_4^{2-})$  present with respect to each other. The relative amounts shown in these tables are to be taken with

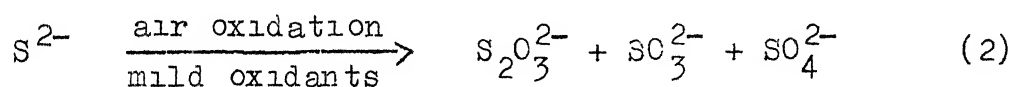
caution since there seems to be considerable overlap between the  $S^{2-}$ ,  $SO_3^{2-}$ , and  $SO_4^{2-}$  elution curves. These, however, do not affect the general conclusion that within a period of 10 days the percentage of  $S^{2-}$ , if originally 100%, in the sample supplied by BARC, dwindles to about 20%, and about 60% of the original  $S^{2-}$  is in the form of products other than  $SO_3^{2-}$  and  $SO_4^{2-}$ .

In view of the above facts the following mechanism is proposed for the reactions undergoing in the radioactive  $S^{2-}$  solution. The following reactions partly explain the decrease in the concentration of sulfide and the build-up of  $SO_3^{2-}$  and the starting of the destruction of  $SO_3^{2-}$  afterwards. The reaction mechanism is as follows.

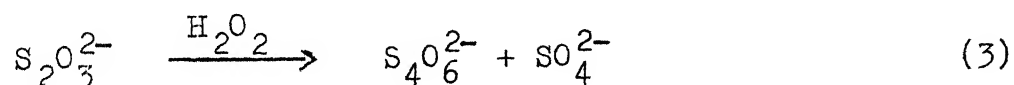
#### Radiolysis of $H_2O$ .



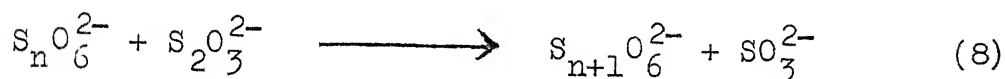
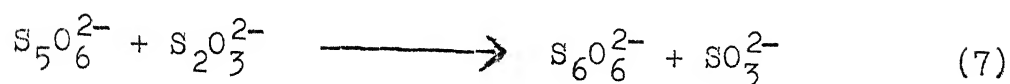
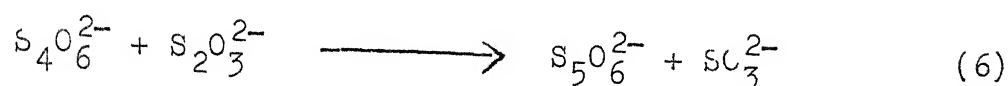
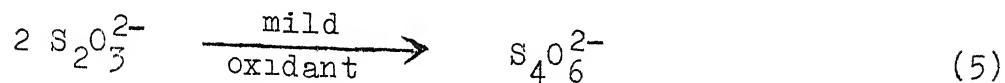
#### Primary reaction :



#### Secondary reactions :



Formation of Polythionates (Sulfane disulfonates).

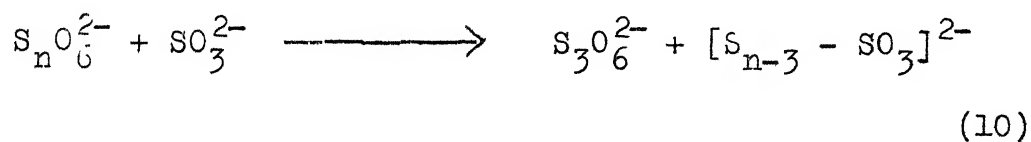


where 'n' is an integer, and  $\text{S}_n\text{O}_6$  represents a polythionate ion.

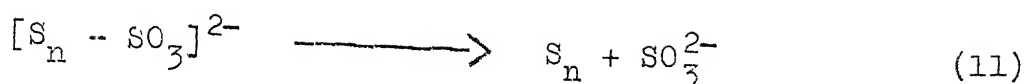
Destruction of higher polythionates (sulfane disulfonates)  
by  $\text{SO}_3^{2-}$  :



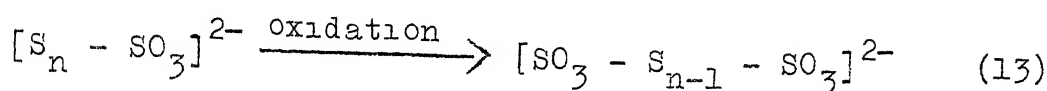
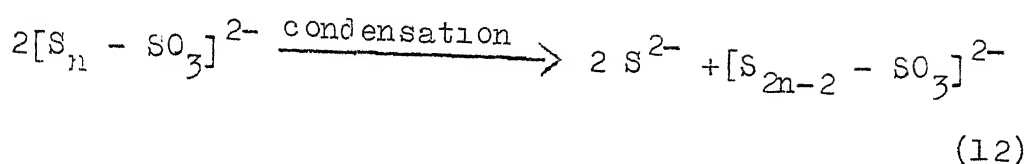
Similarly



Formation of sulfur :



Other reactions of  $[S_n - SO_3]^{2-}$  :



The products of radiolysis of water are well known<sup>21</sup>. The oxidation of sulfide under mild oxidising conditions are also well established<sup>7</sup>. Similarly  $S_2O_3^{2-}$  is easily oxidised by mild oxidising reagents and hence such reactions can be expected to take place under radiolytic conditions in which oxidants like  $H_2O_2$ ,  $\cdot OOH$  and  $\cdot OH$  are formed.

The presence of  $S_2O_3^{2-}$  can lead to the formation of higher polythionates (sulfane disulfonates). Reactions 5, 6, 7 and 8 represent the reactions by which polythionates are formed.

Then the degradation of sulfane disulfonates by sulfite can be explained by the formation of sulfane monosulfonates. For example, the degradation of disulfane disulfonate  $[S_4O_6]^{2-}$  by sulfite is known to produce monosulfane disulfonate  $[S_3O_6]^{2-}$

and thiosulfate  $[S_2O_3]^{2-}$ . This thiosulfate is nothing but the first member of an entirely new class of compounds known as sulfane monosulfonates  $[S_n - SO_3]^{2-}$  in which 'n' is equal to 1. Hence, for the destruction of the higher sulfane disulfonates Schmidt et al.,<sup>22-24</sup> proposed the formation of higher sulfane monosulfonates as the intermediate product. The higher sulfane monosulfonates are very reactive and hence they are destroyed by any one of the above reactions (11, 12 and 13). Further the sulfur ring formation is known to occur through the formation of sulfonates<sup>25</sup>.

The above mechanism is supported by the following experimental facts .

1. Sulfide is consumed rapidly.
2. Sulfite is being formed slowly (Fig. 9).
3. Products other than thiosulfate are formed. This is indicated by more than one peak in the thiosulfate region.
4. After a period of two months (Fig. 12) the amount of sulfite starts decreasing. This may be due to the consumption of sulfite in the destruction of higher polythionates.
5. After 3 months of its preparation visible amount of sulfur is formed. This formation of sulfur is favoured by the formation of higher polythionate<sup>25</sup>.

## CHAPTER 4

### SUMMARY AND SCOPE FOR FUTURE WORK

#### 4.1 Summary

The present work represents the development of an ion-exchange separation method for the analysis of the radiolytic/oxidative products of radioactive sodium sulfide solution and the identification of some of the different species present in the solution as a function of age. The results show that the amount of  $^{35}\text{S}^{2-}$  decreases rapidly and  $^{35}\text{SO}_4^{2-}$  and  $^{35}\text{SO}_3^{2-}$  build-up slowly. After some time the destruction of  $\text{SO}_3^{2-}$  sets in. Further in addition to  $\text{SO}_3^{2-}$ ,  $\text{SO}_4^{2-}$  and  $\text{S}_2\text{O}_3^{2-}$  other species are also present in the solution as early as the 10<sup>th</sup> day after its preparation. This shows that in addition to oxidation by air, beta radiolysis possibly is also playing a major role in the conversion of radioactive sulfide solution into other sulfur products. To explain these facts, a possible reaction mechanism that may be operating in the solution is proposed. From this ion-exchange chromatographic study it is clear that the amount of radioactive  $^{35}\text{S}^{2-}$  decreases very rapidly and hence it is important to know the exact amount of  $^{35}\text{S}^{2-}$  at any given time before using it in any tracer study.

#### 4.2 Scope for Future Work :

Further work can be done to identify the peaks in the thiosulfate region. This will involve the preparation of polythionates in their pure form. Identification of these species

will further confirm the reaction mechanism that is proposed in this thesis. Similar ion-exchange chromatographic analysis can be developed for the commercially available radioactive isotopes in order to determine the possible contamination of a particular oxidation state of the element by other oxidation states. From such a study one will be able to understand the possible reactions and their mechanisms occurring at very low concentrations and it will be of use in basic research in chemistry and nuclear medicine.



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